

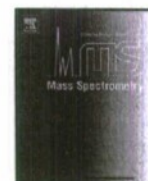
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1. REPORT DATE (DD-MM-YYYY) 10-03 - 2008		2. REPORT TYPE REPRINT		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Reactions of PO_xCl_y^- ions with $\text{O}_2(\text{a}^1\Delta_g)$, H_2O and Cl_2 at 298 K				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHORS Anthony J. Midey*, Itzhak Dotan**, and A.A. Viggiano				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER BM	
				5f. WORK UNIT NUMBER A1	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory/RVBXT 29 Randolph Road Hanscom AFB, MA 01731-3010				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RV-HA-TR-2008-1147	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/RVBXT	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Reprinted from: <i>Int'l J. Mass Spectrometry</i> , 273(2008) 7-10 © 2008, Elsevier, B.V. *Boston College, Chestnut Hill, MA 02467 **NRC Summer Research Fellow. Permanent address: The Open University, Raanana, Israel					
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15. SUBJECT TERMS Excited oxygen Phosphorous oxychlorides Rate constants Branching ratios					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Albert Viggiano
UNCL	UNCL	UNCL	UNL	4	19b. TELEPHONE NUMBER (Include area code)

Reactions of PO_xCl_y^- ions with $\text{O}_2(\text{a } ^1\Delta_g)$, H_2O , and Cl_2 at 298 KAnthony J. Midey¹, Itzhak Dotan², A.A. Viggiano*

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ARTICLE INFO

Article history:

Received 4 February 2008

Accepted 13 February 2008

Available online 10 March 2008

Keywords:

Kinetics

Phosphorus oxychloride

Oxygen singlet delta

Chlorine

Water

ABSTRACT

The rate constants and product branching ratios for the reactions of phosphorus oxychloride anions, PO_xCl_y^- for $x = 1-2$ and $y = 1-3$, with $\text{O}_2(\text{a } ^1\Delta_g)$, Cl_2 , and H_2O have been measured in a selected ion flow tube (SIFT) at 298 K. A mixture of $\text{O}_2(\text{a } ^1\Delta_g)$ in O_2 has been produced using a recently designed chemical singlet oxygen generator (sparger) with an emission detection scheme adopted previously in our laboratory. The experiments continue a series of investigations into the oxidation reactions of PO_xCl_y^- ions, searching for pathways to the terminal PO_2^- and PO_3^- ions observed in combustion chemistry with POCl_3 present. None of the PO_xCl_y^- ions react with H_2O or $\text{O}_2(\text{a } ^1\Delta_g)$. The $\text{O}_2(\text{a } ^1\Delta_g)$ rate constants have a limit of $<1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, except for PO_2Cl^- where a limit of $<5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ has been determined. The H_2O rate constants have limits of $<1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. All of the PO_xCl_y^- ions react with Cl_2 , excluding PO_3^- and PO_2Cl_2^- . Depending on the reactant ion, Cl^- , Cl_2^- or PO_2Cl_2^- product ions form.

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1. Introduction

The oxidation chemistry of O_2 in its first electronic excited state, $\text{O}_2(\text{a } ^1\Delta_g)$, is important in many different processes, including atmospheric infrared emission [1], hydrocarbon combustion [2,3] and oxygen–iodine lasers [4–6]. Reactions of $\text{O}_2(\text{a } ^1\Delta_g)$ with O_2^- and O^- are important in the D-region of the ionosphere because they produce electrons whose concentration affects how radiowaves propagate [7]. A recently implemented emission detection scheme [8] with a small-scale chemical generator for producing singlet oxygen has been used with a selected ion flow tube (SIFT) to study the kinetics of the O^- and O_2^- ionospheric reactions with $\text{O}_2(\text{a } ^1\Delta_g)$ [9]. These experiments have settled previous discrepancies in literature [10–13] and examined the temperature dependencies of the rate constants and product branching ratios from 200 to 700 K [9].

Previously, ions have been shown to decrease the ignition delay time in plasma assisted combustion of hydrocarbon fuels [14,15] and oxyphosphorus compounds have been suggested as viable alternatives to phosphine fuel additives [16]. Consequently, a series of investigations into the oxidation chemistry of phosphorus oxychloride anions of the type PO_xCl_y^- reacting with $\text{O}_2(\text{X}^3\Sigma_g^-)$, O_3 and O atoms has been performed in the SIFT to find routes to the

terminal PO_2^- and PO_3^- ions [17,18], which have been observed in flames when POCl_3 is present [19,20].

Here, we expand upon the previous studies of the oxidation chemistry of PO_xCl_y^- ions [17,18], to measure the rate constants and product ion distributions for the reactions of PO_xCl_y^- ions with $\text{O}_2(\text{a } ^1\Delta_g)$ at 298 K in the SIFT. We utilize a chemical singlet oxygen generator with a sensitive emission detection scheme. Little is known about the reactions of PO_xCl_y^- with Cl_2 or H_2O [21], which are a reactant and a product, respectively, in the chemical generator. Therefore, the reactions of PO_xCl_y^- with Cl_2 and H_2O have also been studied to assess the chemistry that would occur if trace amounts of these species reached the flow tube. Most of the PO_xCl_y^- ions react with Cl_2 ; however, only PO_2Cl^- showed any potential reactivity with $\text{O}_2(\text{a } ^1\Delta_g)$ and none of the ions react with H_2O .

2. Experimental

The measurements were performed at the Air Force Research Laboratory using a SIFT at 298 K. The details of this apparatus have been fully described elsewhere [22]. However, a brief description of the methods pertinent to these studies is given below.

POCl_2^- , POCl_3^- , PO_2Cl^- , and PO_2Cl_2^- were generated in an external electron ionization source by dissociative electron attachment to phosphorus oxychloride (POCl_3 , Aldrich, 99%) [23,24], followed by secondary ion–molecule chemistry [25]. PO_2^- and PO_3^- were generated from dimethyl phosphite (Ventron, 99%). The reactant ion of interest was selected using a quadrupole mass filter and injected through a Venturi inlet into the fast flow of helium buffer gas (AGA, 99.997%) in the flow tube. A roughly 10–15% mixture of $\text{O}_2(\text{a } ^1\Delta_g)$ in O_2 was created using a chemical singlet oxygen

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generator [9] and introduced into the flow tube through a Pyrex inlet with an exterior conductive gold coating to prevent charging in the presence of ions in the flow tube. After reaction over a distance of 49 cm, the product ions and remaining reactant ions were sampled through a nose cone aperture, analyzed with a second quadrupole mass filter and detected by a conversion dynode detector. The kinetics were studied by monitoring the decay of the reactant ion signal as a function of neutral reactant added using a previously measured reaction time. Product branching ratios are determined by extrapolating to zero concentration to account for potential secondary chemistry.

The reactions with Cl_2 (Aldrich, >99.5%) and distilled H_2O were studied using separate 10% mixtures of these reagents in He, which allowed for easier introduction of these species using flow controllers. Rate constants for stable neutral reagents such as these two have relative uncertainties of $\pm 15\%$ with absolute uncertainties of $\pm 25\%$.

The singlet oxygen, $\text{O}_2(a^1\Delta_g)$, was generated in a previously described chemical oxygen generator by bubbling Cl_2 through concentrated aqueous solutions of KOH and H_2O_2 [9]. The resulting gas mixture containing both $\text{O}_2(a)$ and $\text{O}_2(X)$ was passed through a cold trap to remove the H_2O in the mixture that was present partially as a product of the chemical generator and partially as the solvent. Using the SIFT as a chemical ionization detector, we found no Cl_2 to be present in the reactant flow [26]. The gases then flowed through an emission cell, where the 1270 nm emission from the $\text{O}_2(a,0 \rightarrow X,0)$ transition was detected using a calibrated emission detection scheme to determine the absolute $\text{O}_2(a^1\Delta_g)$ concentration that entered the flow tube [8]. Given the additional uncertainties in measuring the absolute concentrations, rate constants for the $\text{O}_2(a^1\Delta_g)$ reactions have relative uncertainties of $\pm 25\%$ and absolute uncertainties of $\pm 35\%$ [9].

The chemical generation scheme is an improvement over the previously used microwave discharge generation scheme [8]. Despite efforts to remove the O, $\text{O}_2(X, v > 0)$ and O_3 produced in the discharge method, small amounts of these highly reactive impurities persist into the flow tube. For slower reactions such as O^- with $\text{O}_2(a)$ where O^- reacts with these contaminants, the required corrections to the rate constants were a sizable fraction of the $\text{O}_2(a)$ rate constant measured [8]. Using the chemical generator eliminated the source of these reactive impurities and produced larger overall concentrations of $\text{O}_2(a)$.

3. Results and discussion

3.1. Reactions with Cl_2

The rate constants and product ions for the reactions of PO_xCl_y^- ions with Cl_2 are given in Table 1 along with the Langevin collision rate constant in units of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The heats of reaction shown in Table 1 have been calculated using 298 K enthalpies pre-

Table 1

Rate constants and product ions for the reaction of PO_xCl_y^- ions with Cl_2 at 298 K measured in a selected ion flow tube (SIFT)

Ion	Products	Rate constant, k [k_{col}] ($\times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	$\Delta H_{\text{rxn}}^{298 \text{ K}}$ (kJ mol $^{-1}$)
PO_2	$\text{Cl} + \text{PO}_2\text{Cl}$	5.0 [8.7]	-113
PO_3	No reaction	<0.01 [8.3]	
POCl_2	$\text{Cl} + \text{POCl}_3$	2.4 [7.6]	-117
POCl_3	$\text{Cl}_2 + \text{POCl}_3$	2.9 [7.3]	-88
PO_2Cl	$\text{PO}_2\text{Cl}_2 + \text{Cl}$	2.7 [7.9]	-166
PO_2Cl_2	No reaction	<0.01 [7.4]	

The rate constant, k , and the Langevin collision rate constant, k_{col} , are given in units of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The heat of reaction at 298 K in kJ mol $^{-1}$ has been calculated using 298 K enthalpies calculated using G3 theory [17,18,27].

viously calculated at the G3 level of theory for both the ions and neutrals [17,18,27]. PO_3^- and PO_2Cl_2^- do not react with Cl_2 . A much larger concentration of pure Cl_2 than $\text{O}_2(a)$ can be introduced into the flow tube; therefore, an upper limit for the rate constant of $<1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ can be made for these ions. The rate constant for PO_2^- is over 50% of the collision rate value, indicating that this reaction is relatively efficient. POCl_2^- , POCl_3^- and PO_2Cl^- react with rate constants around $2\text{--}3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ or an efficiency of about a third. These are typical values observed for other reactions with these ions [17,18,27].

The most common reaction mechanism involves addition of a Cl to the reactant ion, with the electron remaining on the neutral fragment with the higher electron affinity. With PO_2^- and POCl_2^- , the electron is exchanged for the Cl, producing Cl^- and the very stable pentavalent species PO_2Cl and POCl_3 , respectively. Dissociative electron transfer during the formation of Cl^- is highly endothermic for these two reactant ions. PO_2Cl^- gains a Cl, but does not lose its electron, leaving the terminal PO_2Cl_2^- ion with a Cl atom as the neutral fragment. Based on the calculated structures for the reactant and product species [17], adding a Cl to the ion can likely proceed through a complex utilizing a Cl abstraction mechanism. PO_2^- would have to undergo an insertion mechanism on Cl_2 to generate PO_2Cl_2^- . Even though the overall process is 375 kJ mol^{-1} exothermic, the pathway is less likely given that the initial $(\text{PO}_2\text{Cl}_2)^-$ will be a more weakly bound association complex. POCl_3^- reacts only via charge exchange to make Cl_2^- , which may be expected since the electron affinity (EA) of POCl_3 of $\sim 1.5 \text{ eV}$ is less than the EA of Cl_2 of $\sim 2.4 \text{ eV}$ [17,28,29]. PO_2Cl is the only other neutral with an EA less than that for Cl_2 (EA $\text{PO}_2\text{Cl} = \sim 2.1 \text{ eV}$) [17]. However, the charge transfer reaction from PO_2Cl^- is 31 kJ mol^{-1} exothermic, while the observed Cl addition reaction is almost 170 kJ mol^{-1} exothermic. A two step mechanism is possible; charge transfer followed by Cl transfer. No electron detachment from any of the reactant ions has been observed with Cl_2 .

3.2. Reactions with $\text{O}_2(a^1\Delta_g)$ and H_2O

None of the PO_xCl_y^- ions shown in Table 1 reacted with $\text{O}_2(a^1\Delta_g)$, with the possible exception of PO_2Cl^- (see below). For the H_2O reactions, we only studied the species containing both Cl and O and, in all cases, found no reaction. Morris and Viggiano have previously shown that PO_2^- and PO_3^- undergo very slow association with H_2O in the SIFT at 298 K, having upper limits for the bimolecular rate constants of $<1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 0.4 Torr of He [21]. No product ions have been observed in the mass spectra and no measurable decline in the reactant ion signals could be found. Therefore, upper limits of $<1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ can be placed on the rate constants for these reactions with both $\text{O}_2(a^1\Delta_g)$ and H_2O . No change in the nose cone current has been seen either, indicating that associative detachment of electrons does not occur.

PO_2Cl^- is the only ion in this series that reacts with O_2 in its ground state, thereby complicating the study of PO_2Cl^- with $\text{O}_2(a^1\Delta_g)$. Previous studies have shown that PO_2Cl^- reacts with $\text{O}_2(X^3\Sigma_g^-)$ to produce 42% PO_3^- and 58% PO_4^- with a rate constant of $3.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [17]. In the current experiments, the rate constants are measured using a mixture of $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(X^3\Sigma_g^-)$ in the flow tube. The simultaneous rate equations that describe the kinetics in the flow tube during the measurements with PO_2Cl^- are as follows.

$$\frac{\partial[\text{PO}_2\text{Cl}^-]}{\partial t} = -k_{\text{O}_2\text{a}}[\text{PO}_2\text{Cl}^-][\text{O}_2(a)] - k_{\text{O}_2\text{X}}[\text{PO}_2\text{Cl}^-][\text{O}_2(X)] \quad (1)$$

$$\begin{aligned} \frac{\partial[\text{PO}_3^-]}{\partial t} = & f_{\text{O}_2\text{a}}^{\text{O}_2\text{a}} k_{\text{O}_2\text{a}}[\text{PO}_2\text{Cl}^-][\text{O}_2(a)] \\ & + f_{\text{O}_2\text{X}}^{\text{O}_2\text{X}} k_{\text{O}_2\text{X}}[\text{PO}_2\text{Cl}^-][\text{O}_2(X)] \end{aligned} \quad (2)$$

$$\frac{\partial[\text{PO}_4^-]}{\partial t} = f_{\text{PO}_4^-}^{\text{O}_2(a^1\Delta_g)} k_{\text{O}_2(a)} [\text{PO}_2\text{Cl}^-] [\text{O}_2(a)] + f_{\text{PO}_4^-}^{\text{O}_2(X)} k_{\text{O}_2(X)} [\text{PO}_2\text{Cl}^-] [\text{O}_2(X)] \quad (3)$$

In these equations, $k_{\text{O}_2(a)}$ and $k_{\text{O}_2(X)}$ are the total rate constants for PO_2Cl^- reacting with $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(X^3\Sigma_g^-)$, respectively. The branching ratios for generating the PO_3^- products from $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(X^3\Sigma_g^-)$ are given by $f_{\text{PO}_3^-}^{\text{O}_2(a)}$ and $f_{\text{PO}_3^-}^{\text{O}_2(X)}$, respectively, in Eq. (2). Analogous labeling is used for the PO_4^- rate equation shown in Eq. (3).

Eqs. (1)–(3) have been solved and the $\text{O}_2(a^1\Delta_g)$ rate constant and branching ratios varied to best match the experimental data. It is immediately clear that the rate constant for $\text{O}_2(a^1\Delta_g)$ cannot be appreciably larger than that for $\text{O}_2(X)$. If the $\text{O}_2(a^1\Delta_g)$ rate constant was much larger, a faster primary decline at lower concentrations, followed by a slower decline at higher concentrations would be easily discernable, even though the $\text{O}_2(a^1\Delta_g)$ concentration is only ~10–15% of the $\text{O}_2(X)$ concentration. In the reverse situation, where the $\text{O}_2(a^1\Delta_g)$ rate constant is smaller, the decline of the reactant ion would barely change, e.g., it is only 90% of what it would be if all O_2 is in the ground state. This change would not be detectable within our uncertainty. The data show the latter situation to be the case, and our uncertainties show that the $\text{O}_2(a^1\Delta_g)$ rate constant is at most 1.5 times the $\text{O}_2(X)$ rate constant, and possibly much smaller, e.g., $<5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

Analysis of the $\text{PO}_3^-/\text{PO}_4^-$ branching ratios yields some additional limits. If the $\text{O}_2(X)$ branching ratios in Eq. (2) are fixed at the literature values [17] and the two rate constants are set so that $k_{\text{O}_2(a)} = k_{\text{O}_2(X)}$ at the literature value for $\text{O}_2(X)$ [17] then the PO_2Cl^- reaction with $\text{O}_2(a^1\Delta_g)$ will produce nearly 100% PO_3^- . Alternatively, if only $k_{\text{O}_2(X)}$ is fixed at its literature value [17], the solution that reproduces the experimental data gives branching ratios for the reaction with $\text{O}_2(X)$ of 0.48 for PO_3^- and 0.52 for PO_4^- , with the caveats that the $\text{O}_2(a^1\Delta_g)$ reaction is quite slow with $k_{\text{O}_2(a)} \ll k_{\text{O}_2(X)}$ and that no meaningful branching ratios can be derived for the $\text{O}_2(a^1\Delta_g)$ reaction. The new branching ratio values calculated in this way for the $\text{O}_2(X)$ reaction differ slightly from the previous SIFT measurement [17]. However, the difference is within the mutual uncertainties of the two separate experiments. Finally, based on the analysis above, we conclude that the rate constant for the reaction of PO_2Cl^- with $\text{O}_2(a^1\Delta_g)$ is $<5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and, if the rate constant is that large, the amount of PO_3^- produced is between 48 and 100% of the product ions. While these results are not the most definitive, it does show that in the combustion situation outlined in the Introduction, oxidation by the more abundant ground state $\text{O}_2(X)$ will dominate over $\text{O}_2(a^1\Delta_g)$ oxidation.

The very limited reactivity of $\text{O}_2(a^1\Delta_g)$ with the PO_xCl_y^- ions is interesting in comparison to the reactions of O_3 and O [17,18]. Both odd oxygen species have been found to be much better oxidizers with appreciable rate constants for all but the least reactive species. PO_2Cl^- reacts with O , O_2 , and O_3 to form PO_3^- and either PO_2^- (from O) or PO_4^- (from O_2 and O_3). Presumably, these reactions are driven by the extreme stability of the PO_3^- anion. Interestingly, excitation of $\text{O}_2(X)$ to $\text{O}_2(a^1\Delta_g)$ does not increase the rate of oxidation and may, in fact, hamper it. POCl_3^- reacts with O to make POCl_2^- and with O_3 to form the stable species PO_2Cl_2^- , as well as the charge transfer product, O_3^- . POCl_2^- reacts with O to form PO_2Cl^- and with O_3 to mainly form Cl^- . Production of these same product ions from POCl_3^- and POCl_2^- is exothermic with $\text{O}_2(a^1\Delta_g)$, so the bottleneck must come from the details of the potential surface. Such calculations are beyond the scope of the present study. Clearly, breaking the O_2 bond is difficult even for the excited state species.

4. Conclusions

The rate constants and product branching ratios for the reactions of $\text{O}_2(a^1\Delta_g)$, Cl_2 and H_2O with PO_xCl_y^- ions have been measured at 298 K in a SIFT. A mixture of $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(X^3\Sigma_g^-)$ has been created in the SIFT using a newly designed chemical singlet oxygen generator utilizing a calibrated emission detection scheme for $\text{O}_2(a^1\Delta_g)$ [8,9]. The reactions of Cl_2 and H_2O with these anions have also been studied since small amounts of these two species at times entered the flow tube as by-products of the chemical generation method and their reactivity is unknown. However, operating conditions were found for the $\text{O}_2(a^1\Delta_g)$ generator that prevented these interferences from influencing the $\text{O}_2(a^1\Delta_g)$ chemistry.

Except for PO_3^- and PO_2Cl_2^- , all of the ions react with Cl_2 . The main pathway usually involves Cl addition to the reactant ion, except for POCl_3^- which undergoes charge transfer. None of the phosphorus oxychloride ions react with H_2O , except that a weak association reaction has been seen previously with PO_2^- and PO_3^- [21]. Of the PO_xCl_y^- ions, only PO_2Cl^- potentially reacts with $\text{O}_2(a^1\Delta_g)$. Fits to the experimental data show that its rate constant is $<5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [17] and is possibly much smaller than this value.

For models where PO_xCl_y^- ion chemistry must be considered, the negative conclusions of the present results are important findings. The absence of reaction with $\text{O}_2(a^1\Delta_g)$ indicates that these reaction need not be included in simulations of ion-assisted combustion with phosphorus fuel additives. It is apparent that the almost 1 eV of energy available from the first excited electronic state of O_2 is not the overriding factor in controlling the reactivity with these ions.

Acknowledgements

We would like to thank John Williamson and Paul Mundis for their technical support. This work has been supported by the Air Force Office of Scientific Research (AFOSR) under project number EP2303A. AJM is supported under Boston College Contract No. FA8718-04-C-0006. ID was supported under a National Research Council Research Associateship Award at AFRL.

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